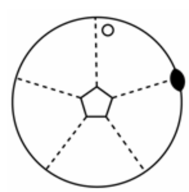
Chemistry 5.04 (F04)
Problem Set 1

Due Monday, 20 September

1. Problem 4.8 in Cotton, p 99.

2. Determine a general matrix representation for σ_v at an angle θ from the xz plane on a point (x_1, y_1, z_1) at angle α from the xz plane.

3. Use the C_5 and C_2 operations on the stereographic projection below to generate a complete mathematical group (the filled-in symbol represents a C_2 axis lying in the page).

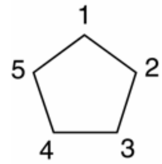


   (a) Do the C_5 and C_2 operators commute? Show by use of the stereographic projection and matrix representations.

   (b) Identify a non-trivial subclass of the mathematical group.

   (c) Determine the classes of the group.

4. Consider the pentagon with labeled vertices.



   (a) Determine the reducible representation for C_5 applied to this basis set.

(b) Determine the block-diagonalized matrix for the C_5 operation using the similarity transformation defined by the matrices below:

$$\vartheta = \begin{vmatrix} 1/\sqrt{5} & 2/\sqrt{10} & 0 & 2/\sqrt{10} & 0 \\ 1/\sqrt{5} & (2/\sqrt{10})\cos 2\pi/5 & (2/\sqrt{10})\sin 2\pi/5 & (2/\sqrt{10})\cos 4\pi/5 & (2/\sqrt{10})\sin 4\pi/5 \\ 1/\sqrt{5} & (2/\sqrt{10})\cos 4\pi/5 & (2/\sqrt{10})\sin 4\pi/5 & (2/\sqrt{10})\cos 2\pi/5 & -(2/\sqrt{10})\sin 2\pi/5 \\ 1/\sqrt{5} & (2/\sqrt{10})\cos 4\pi/5 & -(2/\sqrt{10})\sin 4\pi/5 & (2/\sqrt{10})\cos 2\pi/5 & (2/\sqrt{10})\sin 2\pi/5 \\ 1/\sqrt{5} & (2/\sqrt{10})\cos 2\pi/5 & -(2/\sqrt{10})\sin 2\pi/5 & (2/\sqrt{10})\cos 4\pi/5 & -(2/\sqrt{10})\sin 4\pi/5 \end{vmatrix}$$

$$\vartheta^{-1} = \begin{vmatrix} 1/\sqrt{5} & 1/\sqrt{5} & 1/\sqrt{5} & 1/\sqrt{5} & 1/\sqrt{5} \\ 2/\sqrt{10} & (2/\sqrt{10})\cos 2\pi/5 & (2/\sqrt{10})\cos 4\pi/5 & (2/\sqrt{10})\cos 4\pi/5 & (2/\sqrt{10})\cos 2\pi/5 \\ 0 & (2/\sqrt{10})\sin 2\pi/5 & (2/\sqrt{10})\sin 4\pi/5 & -(2/\sqrt{10})\sin 4\pi/5 & -(2/\sqrt{10})\sin 2\pi/5 \\ 2/\sqrt{10} & (2/\sqrt{10})\cos 4\pi/5 & (2/\sqrt{10})\cos 2\pi/5 & (2/\sqrt{10})\cos 2\pi/5 & (2/\sqrt{10})\cos 4\pi/5 \\ 0 & (2/\sqrt{10})\sin 4\pi/5 & -(2/\sqrt{10})\sin 2\pi/5 & (2/\sqrt{10})\sin 2\pi/5 & -(2/\sqrt{10})\sin 4\pi/5 \end{vmatrix}$$

5. The similarity transformation matrices ϑ and ϑ^{-1} used to solve the problem discussed in Lecture 3 may be extracted from the reducible matrix representations that were used to construct the problem.

(a) Find the three eigenvalues λ_i (i = 1, 2, 3) of the C_3 reducible matrix representation (C_3^{red}) by computing the characteristic polynomial. This is accomplished by solving the secular determinant shown below,

$$\begin{vmatrix} a_{11}-\lambda_i & a_{12} & a_{13} \\ a_{22} & a_{22}-\lambda_i & a_{23} \\ a_{31} & a_{32} & a_{33}-\lambda_i \end{vmatrix}$$

(b) Substitution of the three eigenvalues back into the determinant yields three sets of homogeneous equations of the form,

$$\begin{vmatrix} a_{11}-\lambda_i & a_{12} & a_{13} \\ a_{22} & a_{22}-\lambda_i & a_{23} \\ a_{31} & a_{32} & a_{33}-\lambda_i \end{vmatrix} \begin{vmatrix} x_{1i} \\ x_{2i} \\ x_{3\mathrm{i}} \end{vmatrix} = \begin{vmatrix} 0 \\ 0 \\ 0 \end{vmatrix}$$

(c) The solution to these equations gives an eigenvector for each eigenvalue λ_i. Determine the eigenvectors and normalize them. [Hint: two of the roots are imaginary thus giving two eigenvectors with imaginary components v_1 and v_2…real components my be obtained by taking the following linear combinations v_1(real) = $(v_1 + v_2)/\sqrt{2}$ and $(v_1 - v_2)/\ i\ \sqrt{2}$].

(d) The normalized eigenvectors (i.e. $\langle x_{1i} + x_{2i} + x_{3i} | x_{1i} + x_{2i} + x_{3i} \rangle = 1$ represent the columns of the ϑ matrix. Find the matrix ϑ^{-1} and show that $\vartheta^{-1} \cdot A \cdot \vartheta$ is block-diagonalized (to determine ϑ^{-1}, $(\vartheta^{-1})_{ij} = \chi_{ji}$ / determinant (ϑ)).

(e) Show that the block diagonalized matrix representation for C_3 does not change upon further application character of $\vartheta^{-1} \cdot C_3^{red} \cdot \vartheta$.